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COMPLETE SPECIFICATION

Improvements in or relating to Terpene-Phenol Condensation Products

We, TENNECO CHEMICALS INC., formerly HEYDEN NEWPORT CHEMICAL CORPORATION, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 300 East 42nd Street, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of terpene-phenol condensation products that may be used in the production of polyepoxide resins, and to the products of such process.

It has long been known that a terpene may be reacted with a phenol in the presence of an acid catalyst to form products useful as ingredients of paints, varnishes, and adhesives. The terpene-phenol products that have been described in the literature generally fall into one of three groups: 1) terpene phenyl ethers which result from the reaction of the terpene with the hydroxyl group of the phenol; 2) terpene diphenols which are obtained by reacting one mole of the terpene with two moles of the phenol; and 3) relatively high molecular weight polymeric products. These products may be used directly or following reaction with aldehydes or drying oils in the production of surface coating compositions. They cannot, however, be converted to glycidyl ethers that can be used to form hard, fast drying, durable polyepoxide resin compositions.

According to the present invention there is provided a process for the production of terpene-phenol condensation products having a hydroxyl content of from 7.5% to 8.0% and a molecular weight in the range of from 330 to 360, which process comprises adding a terpene which is a *p*-methadiene, or a terpene convertible under the process condi-

tions to a *p*-methadiene, to a mixture comprising (a) phenol or an alkyl-substituted phenol having from 1 to 3 alkyl groups each containing from 1 to 4 carbon atoms, said phenol or alkyl-substituted phenol being employed in an amount of from 2.25 to 10.0 moles for each mole of terpene, and (b) a catalyst comprising boron trifluoride and/or concentrated sulphuric acid at a temperature in the range of from -10°C. to 15°C. , and maintaining the resulting mixture at said temperature for a time sufficient to form the desired condensation product.

The products of the process of the invention, unlike the terpene-phenol condensation products previously known, can be used to form polyepoxide resin compositions that are characterized by excellent hardness, drying properties, water and chemical resistance, and durability. The terpene-phenol condensation products of the present invention have hydroxyl contents of from 7.5% to 8.0% and molecular weights in the range of from 330 to 360 as determined by the ebullioscopic method. While their exact composition is not at present known, the novel products of the invention appear to be mixtures comprising fifteen or more components which are either terpene-phenol condensation products or terpene polymers and containing as their major constituents a diterpene diphenol and a terpene diphenol.

These novel terpene-phenol condensation products may be used to form relatively low molecular weight glycidyl ethers that can be used in the preparation of heat stable products useful in potting, laminating, and casting applications as well as high molecular weight products which can be reacted with monocarboxylic or dicarboxylic acids or with other polymeric materials to form surface coating compositions. The preparation and properties of the glycidyl ethers are described in detail in our copending Application No. 16914/62, 1012046. In order to obtain

glycidyl ethers that can be used in the preparation of these valuable polyepoxide resin compositions, it is necessary that the terpene-phenol condensation products have hydroxyl contents in the range of from 7.5% to 8.0% and molecular weights in the range of from 330 to 360 as determined by the ebullioscopic method in acetone. Condensation products having hydroxyl contents below 7.5% are comprised principally of terpene phenyl ethers. These materials are difficult to process because of their lower functionality, and they generally form high molecular weight products which have little solubility in or compatibility with the other materials used in the production of polyepoxide resin compositions. On the other hand, condensation products having hydroxyl contents above 8.0%, which contain large amounts of terpene diphenols, form polyepoxide resin compositions that dry slowly to relatively soft films that have poor water and chemical resistance.

The terpenes that may be used in the present invention are the p-methadienes; these include limonene, dipentene, terpinolene, α -terpinene, β -terpinene, γ -terpinene, α -phellandrene, β -phellandrene, 1(7);4(8)-p-methadiene, 2;4(8)-p-methadiene, and 3;8-p-methadiene. A single p-methadiene or a mixture of two or more of these terpenes may be used. In addition, terpenes which are converted to p-methadienes during the course of the condensation may be used; these include, for example, α -pinene, α -terpineol, cineole, terpin hydrate, linalool and geraniol.

The phenolic compounds that are reacted with the terpene to form the novel products of the present invention are phenol and the alkylphenols containing from one to three alkyl groups each containing 1 to 4 carbon atoms. Illustrative of these compounds are resols, xylenols, carvacrol, thymol, and tert. butylphenols. A single phenol or a mixture of phenols may be used. The preferred phenolic compounds are phenol and the cresols.

In carrying out the process of the present invention it is possible to use from 2.25 moles to 10 moles of the phenolic compound for each mole of the terpene. When from 3 moles to 5 moles of the phenolic compound are used per mole of terpene, the optimum yield of the condensation product is obtained. Any of the phenolic compound that does not take part in the condensation reaction may be recovered readily from the product, for example by distillation under reduced pressure.

If the maximum yield of a satisfactory condensation product is to be obtained, the reaction mixture should contain less than 0.5% by weight of water based on the weight of the phenolic compound charged. When more water is present, a low yield of a sticky, hard-to-handle product is ordinarily obtained.

The catalysts that can be used in the preparation of the novel condensation products are boron trifluoride and or sulfuric acid. We prefer to use boron trifluoride in the form of a molecular compound with an organic compound, such as an alcohol, ether, ester, acid or phenol. Illustrative of the organic compounds that may be used to form molecular compounds of boron trifluoride are diethyl ether, dipropyl ether, methyl acetate, acetic acid, propionic acid, ethanol, propanol, phenol and cresol. Particularly good results are obtained using a molecular compound of boron trifluoride and diethyl ether that contains from 45% to 50% of boron trifluoride. Concentrated sulfuric acid and mixtures containing from 50% to 90% of concentrated sulfuric acid and from 10% to 50% of boron trifluoride may also be used to catalyze the condensation. The amount of catalyst that is used generally ranges from 0.5% to 10% and preferably from 1.0% to 3.0% of the total weight of the terpene and phenolic compound in the reaction mixture.

An inert solvent, for example a hydrocarbon or halogenated hydrocarbon, in which both the reactants and products are soluble may be present during the condensation to reduce the viscosity of the reaction mixture and to facilitate the mixing of the reactants. Among the solvents suitable for this purpose are benzene, toluene, xylene, cyclohexane, chloroform, carbon tetrachloride, and ethylene chloride.

The reaction between the terpene and the phenol to give the novel condensation products is preferably effected by adding the terpene slowly to a mixture of the phenol, catalyst and solvent and then allowing the reaction mixture to stand for several hours at a suitable temperature before the isolation of the condensation products is begun. Procedures calling for the addition of the phenol and terpene to the catalyst solution or for the addition of the catalyst to a mixture of the other reactants generally yield terpene-phenol condensation products that differ substantially from the novel condensation products in such critical properties as hydroxyl content and molecular weight.

To obtain products having hydroxyl contents and molecular weights in the desired range, it is necessary that the condensation be carried out at a temperature between -10°C. and 15°C. , and preferably between 0°C. and 5°C.

The condensation product may be separated from the other components of the reaction mixture by well-known procedures. For example, the catalyst may be removed from the reaction mixture by washing with water or with a dilute salt solution; the solvent may be removed by distillation; and unreacted phenol and other volatile materials present in the reaction mixture may be removed by

distillation under subatmospheric pressure.

Terpene-phenol products prepared in accordance with the process of this invention are generally pale yellow in color. Products having lighter colors may be obtained by carrying out the condensation in an atmosphere of an inert gas, such as nitrogen, and in the presence of adsorbents, such as carbon, diatomaceous earth, and fuller's earth.

The following examples are illustrative of the manner in which the terpene-phenol condensation products of this invention may be prepared. It is to be understood, however, that these examples are not to be construed as being limitative but are furnished merely for the purpose of illustration.

EXAMPLE 1

A mixture of 846 grams (9.0 moles) of phenol, 34 grams (0.236 mole) of a molecular compound of boron trifluoride and diethyl ether which contained 47% by weight of boron trifluoride, 750 ml. of benzene, 10 grams of diatomaceous earth, and 10 grams of activated carbon was placed in a flask equipped with an agitator, thermometer, gas inlet tube, and addition funnel. To this mixture which had been cooled to 5°C. was added 272 grams (2 moles) of dipentene over a period of two hours during which the mixture was agitated constantly and maintained at 5°C. The reaction mixture was then agitated at 5°C. for two hours. The addition of the dipentene and the condensation reaction were carried out in an atmosphere of nitrogen. Following the addition of 500 ml. of water to the reaction mixture, the aqueous layer that resulted was separated and discarded. The organic layer was washed with four 500 ml. portions of water and then distilled under atmospheric pressure to remove the benzene. The residue was distilled at 3 mm. pressure until a temperature of 180°C. was reached. The resulting dipentene-phenol condensation product, which weighed 367 grams, was poured onto a stainless steel sheet, cooled, and broken into small pieces. It had a hydroxyl content of 7.96%, molecular weight (ebullioscopic method in acetone) of 344, and Gardner color of 2.75.

EXAMPLE 2

A mixture of 131 pounds of benzene, 169 pounds of phenol, and 6.5 pounds of a molecular compound of boron trifluoride and diethyl ether which contained 47% by weight of boron trifluoride was cooled to 5°C. Then 54 pounds of dipentene was added over a period of 4.75 hours during which time the mixture was agitated constantly and maintained at 5°C. The reaction mixture was stirred at 5°C. for two hours after which time 100 pounds of a 12% aqueous salt solution was added to it. The resulting aqueous layer was separated and discarded. The

organic layer was washed with five 100 pound portions of a 12% aqueous salt solution and then distilled under atmospheric pressure to remove the benzene. The residue was distilled at 17 mm. pressure to a temperature of 180°C. to remove unreacted phenol and other volatile materials. The resulting dipentene-phenol condensation product, which weighed 97 pounds, had a hydroxyl content of 7.88% and a molecular weight (ebullioscopic method in acetone) of 339.

EXAMPLE 3

A mixture of 846 grams (9.0 moles) of phenol, 750 ml. of benzene, and 34 grams (0.235 mole) of a molecular compound of boron trifluoride and diethyl ether that contained 47% by weight of boron trifluoride was cooled to 5°C. To this mixture was added 272 grams (2.0 moles) of citrus limonene over a period of 90 minutes during which time the mixture was maintained at 5°-6°C. The mixture was then agitated at 2°-5°C. for 2 hours. Following the addition of 300 ml. of water, the aqueous layer that resulted was separated and discarded. The organic layer was washed with four 500 ml. portions of water and then distilled under atmospheric pressure to remove the benzene. The residue was distilled under reduced pressure to a temperature of 180°C. to remove unreacted phenol and other volatile materials. The resulting limonene-phenol condensation product, which weighed 508.5 grams, was a pale yellow glass which had a hydroxyl content of 7.68% and a molecular weight of approximately 340.

EXAMPLE 4

An α -pinene-phenol condensation product was prepared by the procedure of Example 3 using 846 grams of phenol and 272 grams of α -pinene. The product, which weighed 472 grams, had a hydroxyl content of 7.50% and a molecular weight of approximately 340.

EXAMPLE 5

A dipentene-o-cresol condensation product was prepared by the procedure of Example 3 using 860 grams of o-cresol and 272 grams of dipentene. The product, which weighed 602 grams, had a hydroxyl content of 7.8% and a molecular weight of approximately 350.

EXAMPLE 6

A mixture of 423 grams (4.5 moles) of phenol, 375 ml. of benzene, and 40 grams of concentrated sulfuric acid was cooled to 5°C. To this mixture was added 136 grams (1.0 mole) of dipentene over a period of 90 minutes during which time the reaction mixture was maintained at 5°C. The reaction was then agitated at 5°C. for 2 hours. Following the addition of 150 ml. of water, the aqueous layer that resulted was separated and dis-

carded. The organic layer was washed with four 250 ml. portion of water and then distilled under atmospheric pressure to remove the benzene. The residue was distilled under reduced pressure (10 mm.) to a temperature of 180°C. to remove unreacted phenol and other volatile materials. The resulting dipentene-phenol condensation product, which weighed 253 grams, had a hydroxyl content of 7.5%, and a molecular weight in the range 330 to 360.

EXAMPLE 7

The procedure of Example 6 was repeated using as catalyst a mixture containing 4.25 grams of a boron trifluoride-diethyl ether molecular compound and 17.5 grams of concentrated sulfuric acid. There was obtained 243 grams of a dipentene-phenol condensation product which had a hydroxyl content of 7.5% and a molecular weight in the range 330 to 360.

EXAMPLE 8

A mixture of 846 grams (9.0 moles) of phenol, 750 ml. of benzene, and 59 grams

of a molecular compound of boron trifluoride and phenol that contained 26% by weight of boron trifluoride was cooled to 5°C. To this mixture was added 272 grams (2.0 moles) of dipentene over a period of 90 minutes during which time the mixture was maintained at 5°C. The reaction mixture was then agitated at 5°C. for 2 hours. The condensation product was isolated by the procedure described in Example 3. There was obtained 486 grams of a dipentene-phenol condensation product which had a hydroxyl content of 7.60% and a molecular weight in the range 330 to 360.

EXAMPLE 9

To demonstrate the effect that water may have on the yield and quality of the condensation products, a series of experiments was carried out in which the water content of the reaction mixture ranged from 0.12% to 3% based on the weight of the phenol charged. In each case the procedure described in Example 8 was followed. The results obtained are summarized in the table that follows:

Experiment	Water Content (% based on weight of phenol charged)	Yield	Hydroxyl Content of Product	Appearance
A	3	16.5%	4.7%	Sticky, semi-solid
B	0.9	45.3%	—	Semi-solid which could not be flaked
C	0.12	77%	7.8%	Flaked solid product

WHAT WE CLAIM IS:—

1. A process for the production of terpene-phenol condensation products having a hydroxyl content of from 7.5% to 8.0% and a molecular weight in the range of from 330 to 360, which process comprises adding a terpene which is a *p*-methadiene, or a terpene convertible under the process conditions to a *p*-methadiene, to a mixture comprising (a) phenol or an alkyl-substituted phenol having from 1 to 3 alkyl groups each containing from 1 to 4 carbon atoms, said phenol or alkyl-substituted phenol being employed in an amount of from 2.25 to 10.0 moles for each mole of terpene, and (b) a catalyst comprising boron trifluoride and/or concentrated sulphuric acid at a temperature in the range of from -10°C. to 15°C., and maintaining the resulting mixture at said temperature for a time sufficient to form the desired condensation product.
2. A process according to Claim 1, wherein

from 3 to 5 moles of said phenol or alkyl-substituted phenol are used for each mole of terpene.

3. A process according to Claim 1 or 2, wherein said temperature is in the range of from 0°C. to 5°C.

4. A process according to Claim 1, 2 or 3, wherein the terpene is dipentene, limonene or α -pinene.

5. A process according to Claim 1, 2, 3 or 4, wherein the alkyl-substituted phenol is a cresol.

6. A process according to any one of Claims 1 to 5, wherein the catalyst comprises boron trifluoride which is employed as a molecular compound with an ether, alcohol, ester, acid or phenol.

7. A process according to Claim 6, wherein the boron trifluoride is employed as a molecular compound of boron trifluoride and diethyl ether, said molecular compound containing from 45% to 50% by weight of

boron trifluoride.

5 8. A process according to any one of the preceding Claims, wherein the catalyst comprises a mixture of from 50% to 90% by weight of concentrated sulphuric acid and from 10% to 50% by weight of boron trifluoride.

10 9. A process according to any one of the preceding Claims, wherein said catalyst is employed in an amount of from 1.0% to 3.0% by weight, based on the total weight of terpene and phenol or alkyl-substituted phenol.

15 10. A process according to any one of the preceding Claims, wherein the condensation reaction is carried out in the presence of an inert solvent.

20 11. A process according to Claim 10, wherein said solvent is benzene, toluene, xylene, cyclohexane, chloroform, carbon tetra-

chloride or ethylene chloride.

12. A process according to any one of the preceding Claims, wherein the reaction mixture contains less than 0.5% by weight of water, based on the weight of phenol or alkyl-substituted phenol employed. 25

13. A process for the production of a terpene-phenol condensation product substantially as described in any one of the foregoing Examples 1 to 8. 30

14. A terpene-phenol condensation product whenever prepared by the process claimed in any one of the preceding Claims.

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